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A Molecular Beam Study of the Thermal Dissociation of 1,4-Butane Diammonium Dinitrate

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The thermal decomposition of BDD has been observed in a TOF - quadrupole tandem mass spectrometer system. The major ion products observed were 30, 41, 43, and 46 amu. All of the data obtained in the present study indicate that, under vacuum, BDD thermally decomposes at temperatures in the range of 160-180°C to produce BDA and nitric acid. The nitric acid partially decomposes to produce nitrogen dioxide. Since all products are volatile, the solid residue after heating is pure BDD.				
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PREFACE

This report describes the work performed by personnel at the Department of Physics, Florida International University, Primera Casa 115, Tamiami Campus, Miami, Florida 33199, during the period May 1986 to September 1987. The contract program manager was Dr John W. Sheldon and the AFATL program manager was Dr Robert L. McKenney Jr. Funding was provided by the Air Force Armament Laboratory, Armament Division, Energetic Materials Branch, Eglin Air Force Base, Florida 32542-5434, under Contract F08635-86-K-0212.

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I. Introduction

A molecular beam represents the ideal interface between a chemical reaction and product detection and identification.¹ With a background pressure of the order of 10^{-6} Torr the chemical identity of the product species and their relative concentrations are preserved down the beam path. By modulating the beam the detection system can discriminate against background molecules produced by secondary reactions elsewhere in the vacuum system.^{2,3} Analysis of the leading edge of a modulated molecular beam signal has been used to determine the translational temperature of the beam.⁴

Herein we report on the pyrolysis of BDD (1,4-butane diammonium dinitrate) using a molecular beam sampling system designed for both phase lock-in measurement and full TOF (time-of-flight) velocity analysis of the mass spectrometer detected molecular products beam. In the single reaction cell configuration the beam effuses from a Knudsen flow reaction cell which contains thermally decomposing and subliming BDD. The TOF analysis allows determination of the molecular mass the detected ion mass traveled on down the beam path. In the two cell configuration the product gases from the thermal decomposition and sublimation in the source cell pass into a second Knudsen cell where secondary decompositions at higher temperatures are observed. With this arrangement only lock-in measurement of the ion signal is employed.

In the following section the apparatus design is described in detail and in section III the experimental procedure is presented. The observed decompositions are reported in the section IV for both the single and double cell configurations. Results of running BDD in

standard FAB (fast atom bombardment) and EI (electron bombardment ionization) mass spectrometers are also given in section IV. All results are discussed in section V and conclusions presented in section VI. Preliminary runs with the apparatus to look at the well understood thermal decomposition of malonic acid⁵⁻⁸ were used to check the concept of the experiment. These tests will be described elsewhere.⁹ A derivation of the TOF distribution function, Eq.(1), in section III is presented in the Appendix.

II. Apparatus

A schematic drawing of the single source cell molecular beam apparatus is presented in Fig.1(a) and the double cell arrangement is shown in Fig.1(b). For both cases the typical background pressure in the main chamber is 2×10^{-6} Torr and in the quadrupole chamber it is 2×10^{-7} Torr. In the single reaction cell configuration shown in Fig.1(a) thermal decomposition and sublimation takes place in the reaction cell (R) and gaseous products effuse through slit S_1 . The volume of the reaction cell, which is contained in an aluminum oven, is approximately 1.0 cm^3 . This volume allows sufficient wall collisions for thermal translational equilibrium of product molecules.¹⁰ The reaction cell pressure is typically less than 1.0 milliTorr as measured by an electronic capacitance manometer. This low pressure keeps the mean free path of product molecules greater than the cell dimensions, thereby minimizing the effect of secondary bimolecular reactions. The ovens containing the source and reaction cells are heated by resistance heaters on either side of the cells and the oven assemblies are supported on and thermally insulated by 4, 4-40 stainless steel machine

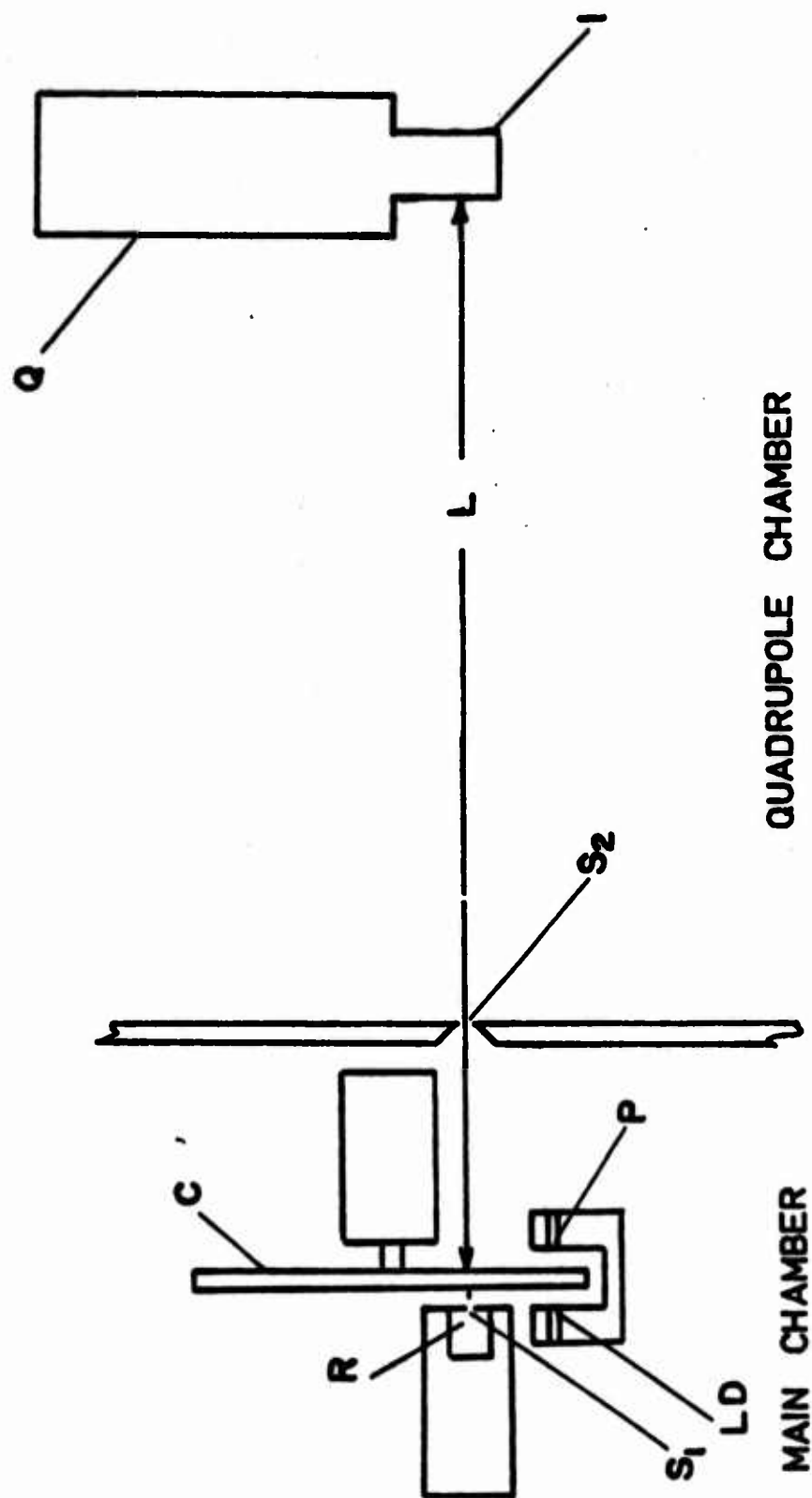


Figure 1(a). Molecular Beam Sampling System. C, chopper wheel; I, electron bombardment ion source; L, beam path length, 31.7 cm; LD, light emitting diode; P, photo-transistor; Q, quadrupole mass spectrometer; R, reaction cell; S₁, reaction cell exit slit; S₂, collimation slit

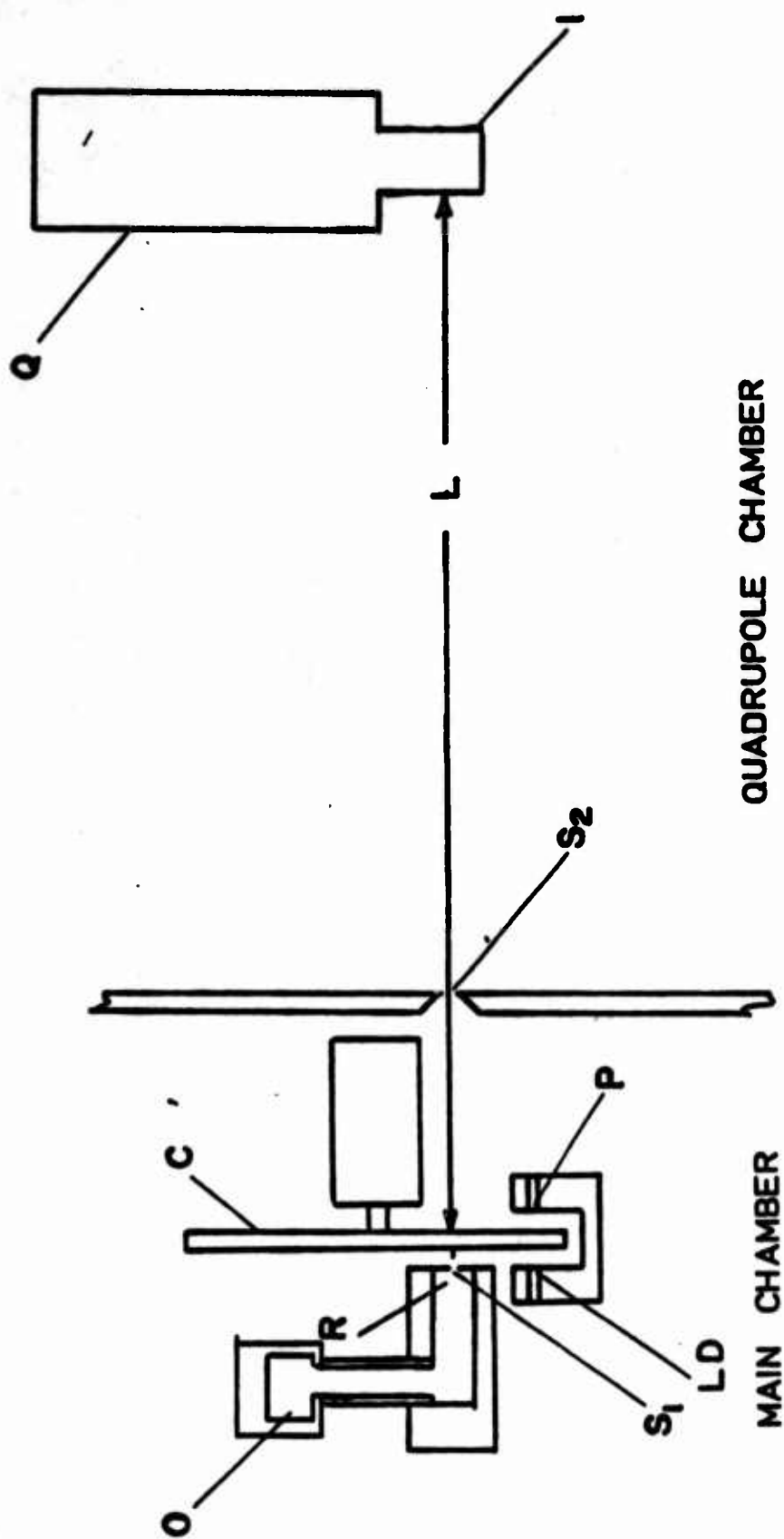


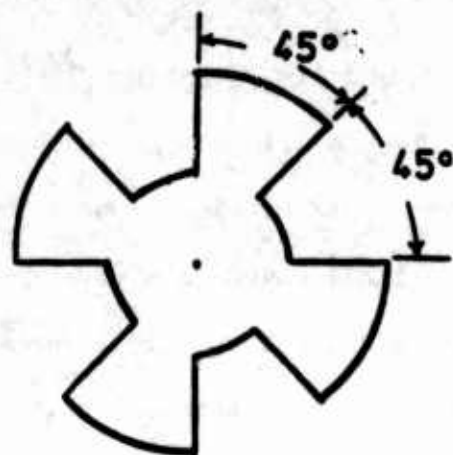
Figure 1(b). Molecular Beam Sampling System, Double Oven

Configuration. O, source oven

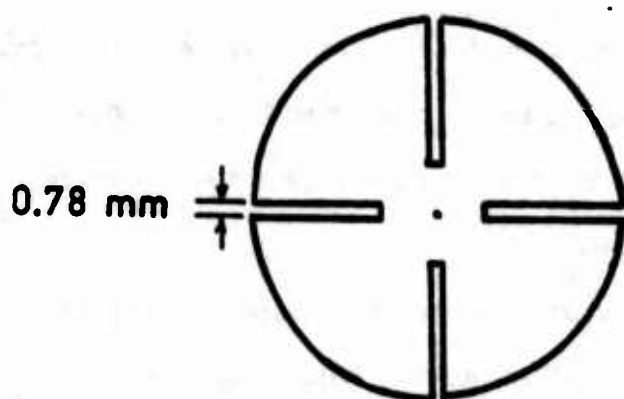
screws approximately 3 cm. long. In operating with a single cell as shown in Fig.1(a) the reaction cell is charged with 100- 200 milligrams of sample. When the two oven configuration is used the charge is placed in the source cell (see Fig.1(b)) which is always operated at a lower temperature than the reaction cell. This allows investigation of the decomposition at higher temperatures, whereas in the single cell configuration the sample would be rapidly expended and the cell pressure would be too high to neglect bimolecular collisions and maintain Knudsen flow. The oven temperatures are measured by iron-constantan thermocouples embedded in the oven walls. The sample temperature is measured in the single cell case by a thermocouple embedded directly in the sample.

The beam path length, L is 31.7 cm, and the chopper operates at 60 rps with 4 equally spaced slits which allows full reception of each TOF distribution without overlap of signal from the following slit. The three chopper wheels shown in Fig.2 were fabricated from 0.84 mm sheet aluminum with different slit widths so that the best compromise between mass resolution (higher for narrow slit widths) and count rate (higher for larger slit widths) could be achieved in a given measurement.

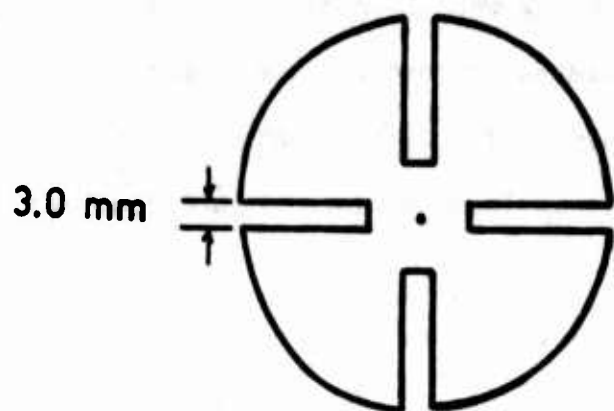
Ions are produced from beam molecules by electron bombardment ionization in the ion source of the quadrupole mass spectrometer (Micromass 200). This instrument has been modified to admit the beam from the side rather than the end of the source to avoid having beam gases accumulate down the ion path. The ion source electronics have also been modified to provide for variation of the electron accelerating potential. Determinations of the appearance potentials of



A



B



C

Figure 2. Chopper Wheels

the background gases indicate the system has an energy resolution of ± 1.0 electron-volts. Ions produced in the source pass through the spectrometer and into a channeltron electron multiplier. The channeltron output signal is detected either by (1) measuring the voltage produced in the preamplifier which is in phase with the chopper wheel using the lock-in amplifier (Princeton Applied Physics Corp. Model HR-8) or (2) by counting pulses from the channeltron electron multiplier using a computer based multichannel analyzer system.¹¹

A diagram of the electronic system used for TOF analysis is shown in Fig.3. The slit in the chopper wheel is illuminated with a light emitting diode and the resulting light pulse is detected with a photo-transistor. The voltage pulse from the photo-transistor is amplified and used both to start the time base and to generate a pulse that can be added to the accumulated data to mark the start of the chopper open time. The output ramp of the time base generator is applied to the input of a linear gate module. The channeltron output pulse is amplified and applied to a single channel analyzer used in the discriminator mode, whose output triggers a gate generator that opens the linear gate. The output pulse from the linear gate has an amplitude proportional to the time between the chopper opening and the reception of a mass analyzed molecular ion by the channeltron. These pulses are accumulated in a computer based pulse height analyzer (Tracor Northern TN-11).

III. Experimental Procedure

The BDD used in the present work was made in our laboratory from BDA (1,4-butanediamine) obtained from the High Explosive Research

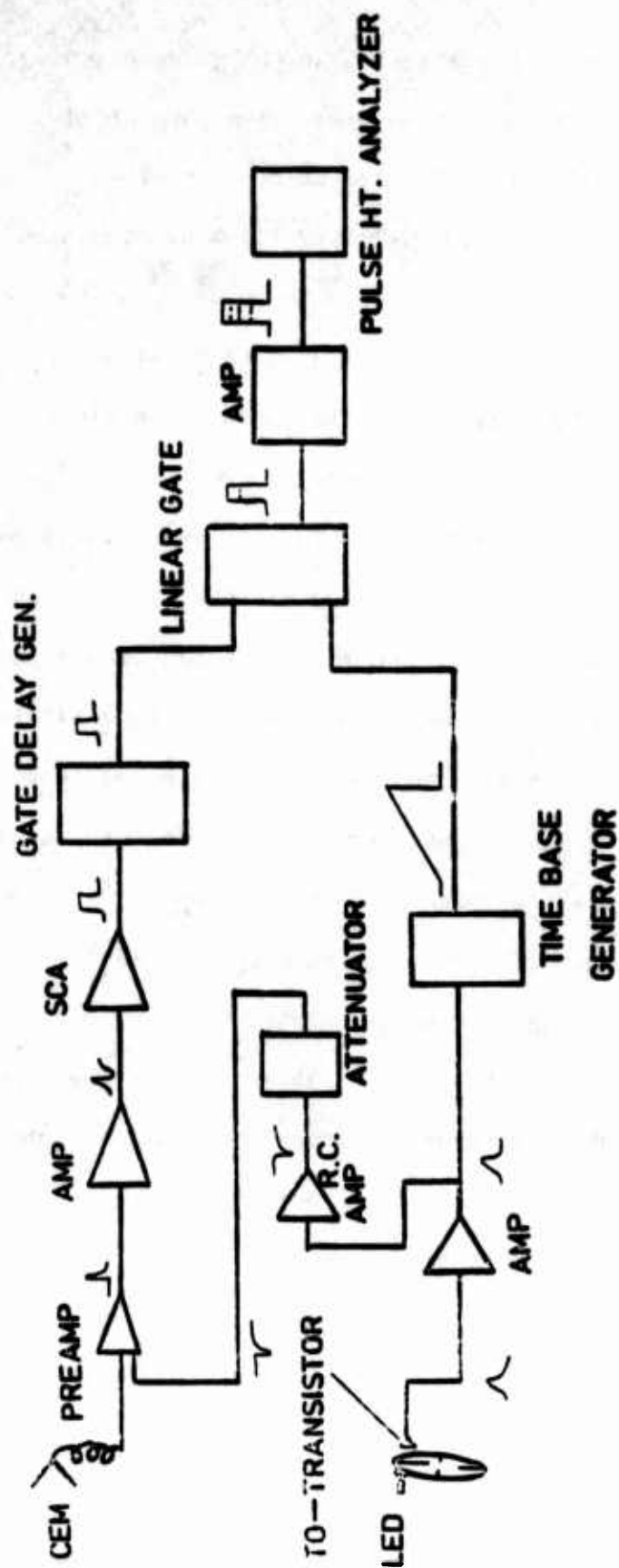


Figure 3. TOF Electronics

and Development group at Eglin Air Force Base, FL. A solution of BDA in absolute ethanol was placed in a 3-neck round bottom flask equipped with a thermometer, nitrogen inlet and dropping funnel with pressure equalizing sidearm. The solution was stirred, and cooled to 0 C in an ice salt bath, and the apparatus was purged with nitrogen. Concentrated nitric acid (ca 2.5 equiv) was added dropwise at such a rate that the temperature in the flask did not rise above 20 C. The product, a white precipitate, was filtered and washed with ice cold ethanol. The product was recrystallized from warm ethanol and stored either in a desiccator or in a freezer (ca -20 C). Characterization was effected by IR spectroscopy.¹² The significant peaks are given in Table I.

All data were obtained with an electron accelerating potential of 70 volts except as noted when determining appearance potentials. The initial data were taken using chopper wheel A (see Fig.2) and the signal was detected with the lock-in amplifier or the TOF system in the computer controlled gated scaler mode. In this mode, counting gates were set as shown in Fig.4 in order to distinguish the beam signal from the background. Scans of this signal as a function of ion mass, M , and sample temperature were run. For the most intense ion mass signals, intensity versus temperature data were obtained to measure activation energy. For the two masses with the highest signal strength ($M=30,46$) the electron bombardment potential was varied to obtain appearance potentials. Next, for the three strongest ion mass signals, chopper wheels B and C (see Fig.2) were used to measure TOF distributions.

The experimental TOF distributions for a given ion mass, $I_M(t)$ are fitted to the functional form (see the Appendix)

Table I - BDD IR¹²

peak wave number (cm ⁻¹)	identification
1385	N - O Symmetric Stretch
1590	weak N-H asymmetric bend
2900	C-H stretch
3400 - 2300	+ NH ₃ stretch

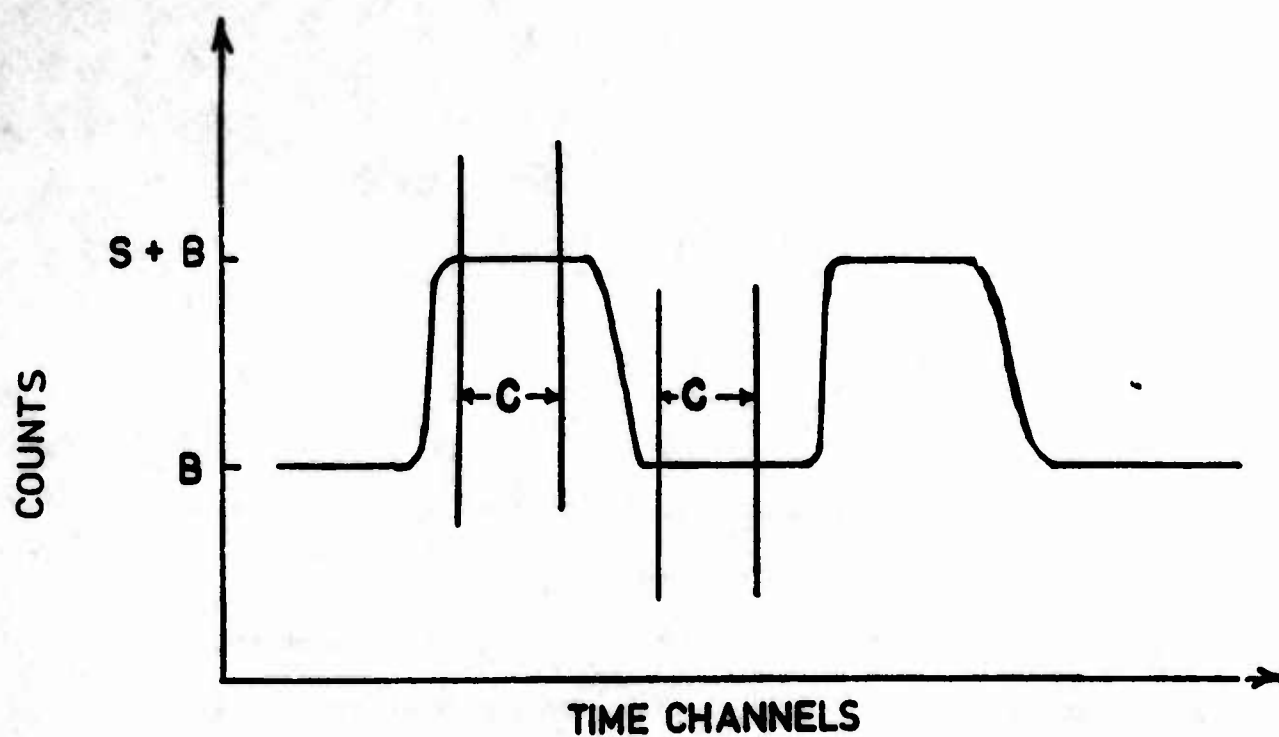


Figure 4. Beam Signal with Chopper A Showing the Gated Scalar Mode

Signal (S) + background (B) and background are obtained by adding counts over C channels in the intervals shown

$$I_M(t) = \sum_{i=1}^N I_i f_i(t) + I_b \quad (1)$$

where

$$f_i(t) = \left[\frac{1}{(t-T)} \exp\left(- \frac{L^2}{\alpha_i^2 (t-T)^2} \right) - \frac{1}{t} \exp\left(- \frac{L^2}{\alpha_i^2 t^2} \right) \right. \\ \left. + \frac{\sqrt{\pi} \alpha_i}{2L} \left\{ \operatorname{erf}\left(\frac{L}{\alpha_i t} \right) - \operatorname{erf}\left(\frac{L}{\alpha_i (t-T)} \right) \right\} \right]$$

and $\alpha_i = \sqrt{2KU/m_i}$, U is the gas temperature, T is the chopper open time, I_i is the intensity constant of the product mass m_i and I_b is the background signal intensity. This function describes the measured intensity distribution for N product masses in the beam, each of which could produce the ion mass M . The derivation of Eq.(1), which is given in the Appendix, is based on the following assumptions:

1. The velocity distribution in the reaction cell is Maxwellian.
2. The beam is not scattered by background gas in the vacuum chamber which would preferentially attenuate low velocity molecules.
3. The electron bombardment ionization efficiency in the mass spectrometer is inversely proportional to the beam molecule velocity.
4. The chopper transmission function is rectangular, that is the transmitted intensity is a constant during the open time and zero for other times.

The TOF data were analyzed by the method of linear least squares¹³ to determine the I_i and I_b with the summation in Eq.(1) extending over all N masses thought to be chemically probable. While this procedure does not give unique solutions, it can be used as a guide in the

identification of products.

IV. Results

All data were obtained with the single oven configuration (Fig.1(a)) unless specifically noted otherwise. The BDD mass spectra observed with our lock-in amplifier measurement system using the single oven configuration (Fig.1(a)) are presented in Fig.5. Signal intensities in Fig. 5 are normalized to the intensity of mass 18 in the mass range 0-20 amu, mass 30 in the range 20-35 amu and mass 46 in the range 35-50 amu. The product ion mass spectra are relatively constant over the temperature range from 160 to 180 C.

The TOF system was then used in the gated scaler mode to measure the ion intensity as a function of temperature for $M = 30, 41, 43$ and 46 amu. These data are presented in Fig.6 on semi-log plots which facilitate determination of the activation energy, E_M for each ion's production. The data are least squares fitted to a straight line and the results are summarized in Table II. The activation energies for the production of ion masses 30 and 41 amu are equal, and the activation energies for ion masses 43 and 46 amu are equal within the experimental error.

Ion signal intensity as a function of electron accelerating potential is shown in Figs.7(a) and 7(b) for ion masses of 30 and 46. Appearance potentials estimated from the extrapolated intercepts are 13.0 ± 0.5 and 13.5 ± 1.5 electron volts respectively.

For ion masses of 30, 43 and 46 amu full TOF distributions using chopper C (Fig4) are reported in Figs.8,9 and 10. The vertical error bars represent the statistical uncertainty and the horizontal error

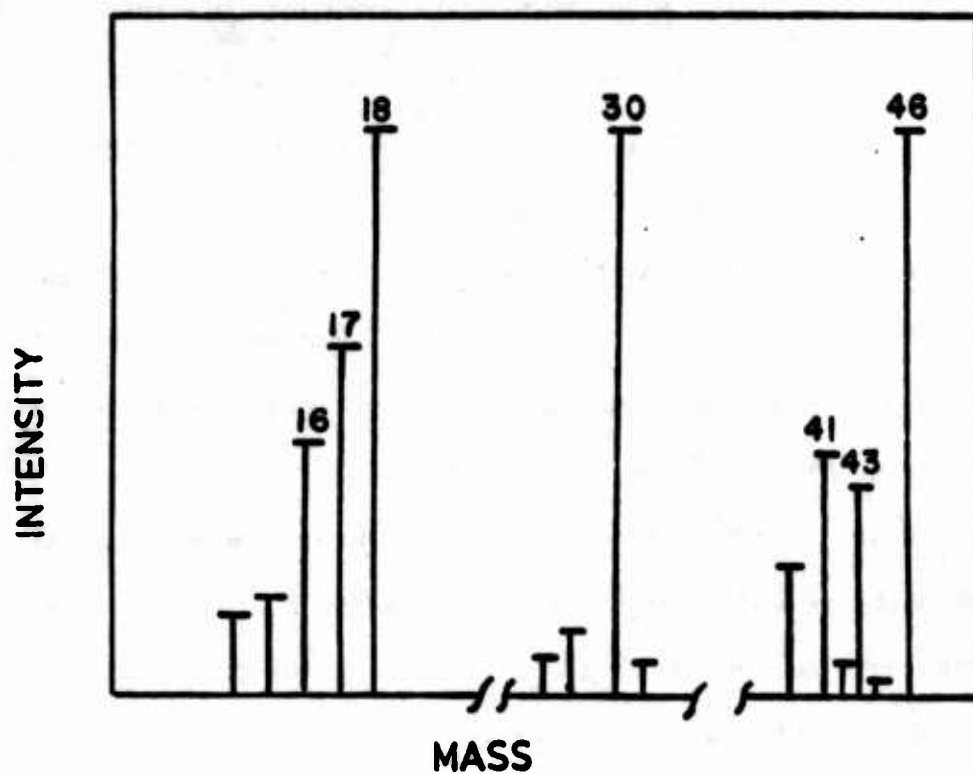


Figure 5. BDD Mass Spectrum Obtained in the Gated Scalar Mode Using Chopper A; Reaction Cell Temperature, 180°C

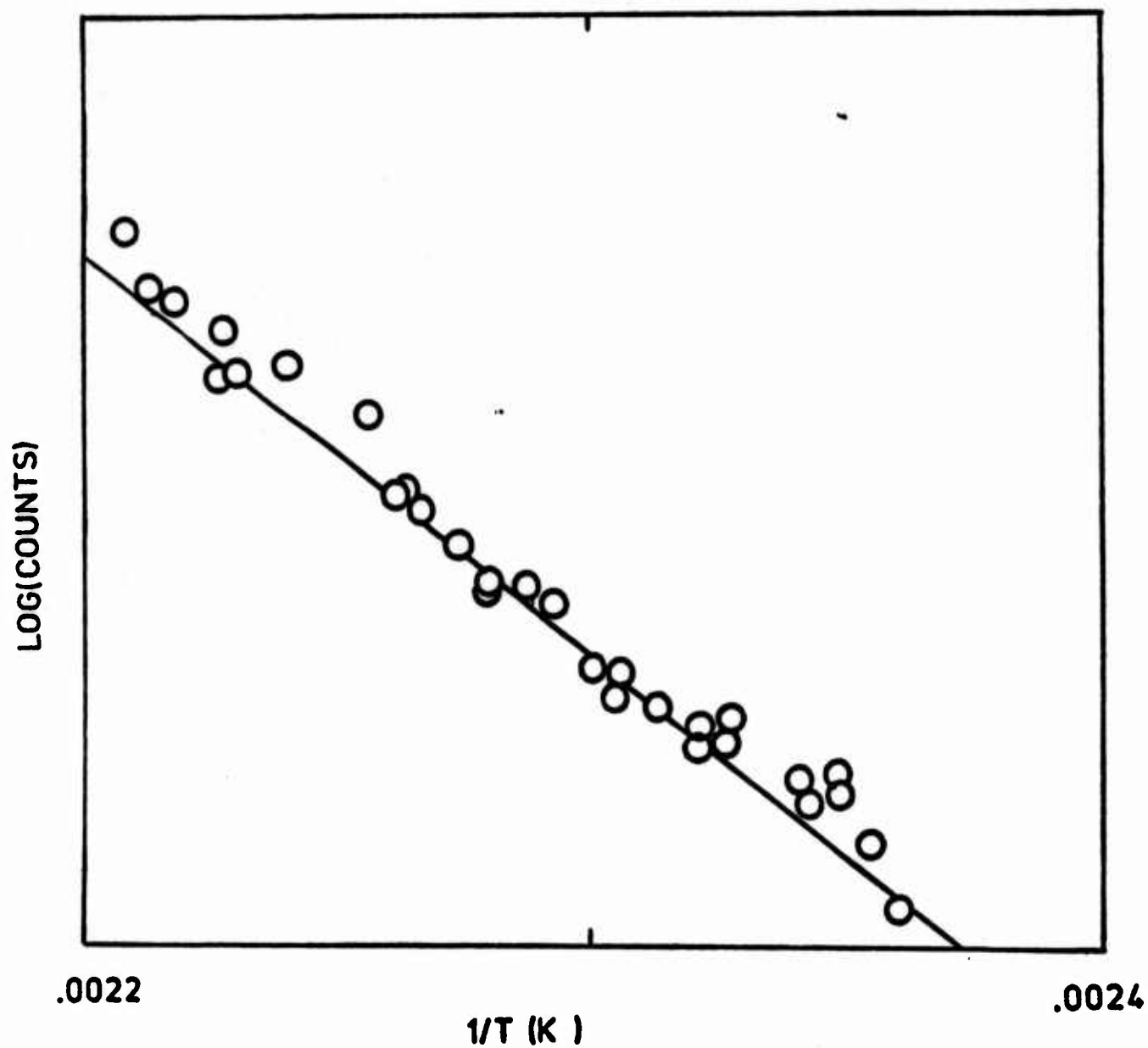


Figure 6. Activation Energy Plots in the Gated Scalar Mode

(a). Ion Mass = 30.

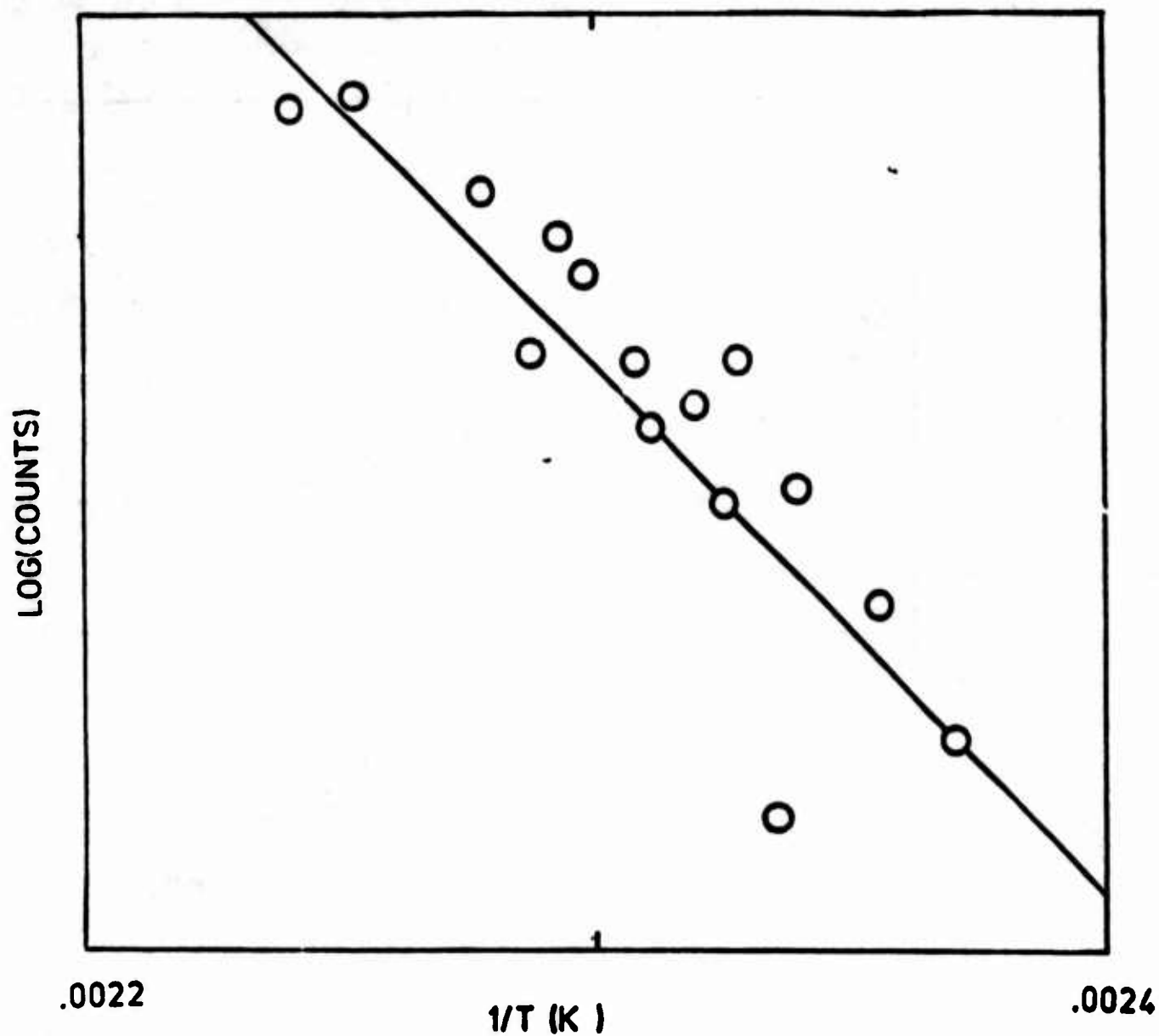
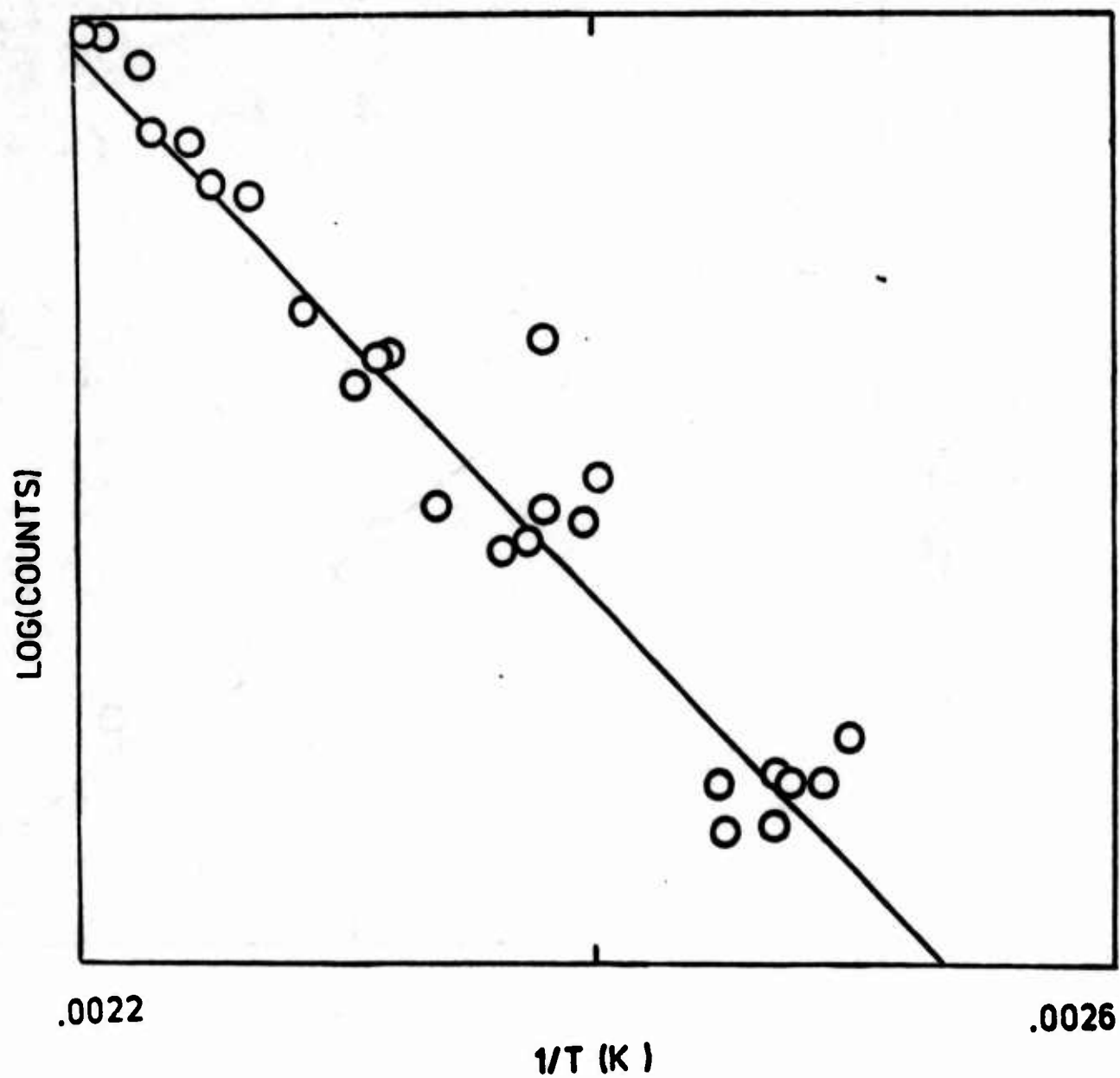


Figure 6. Activation Energy Plots in the Gated Scalar Mode (Continued)

(b). Ion Mass = 41



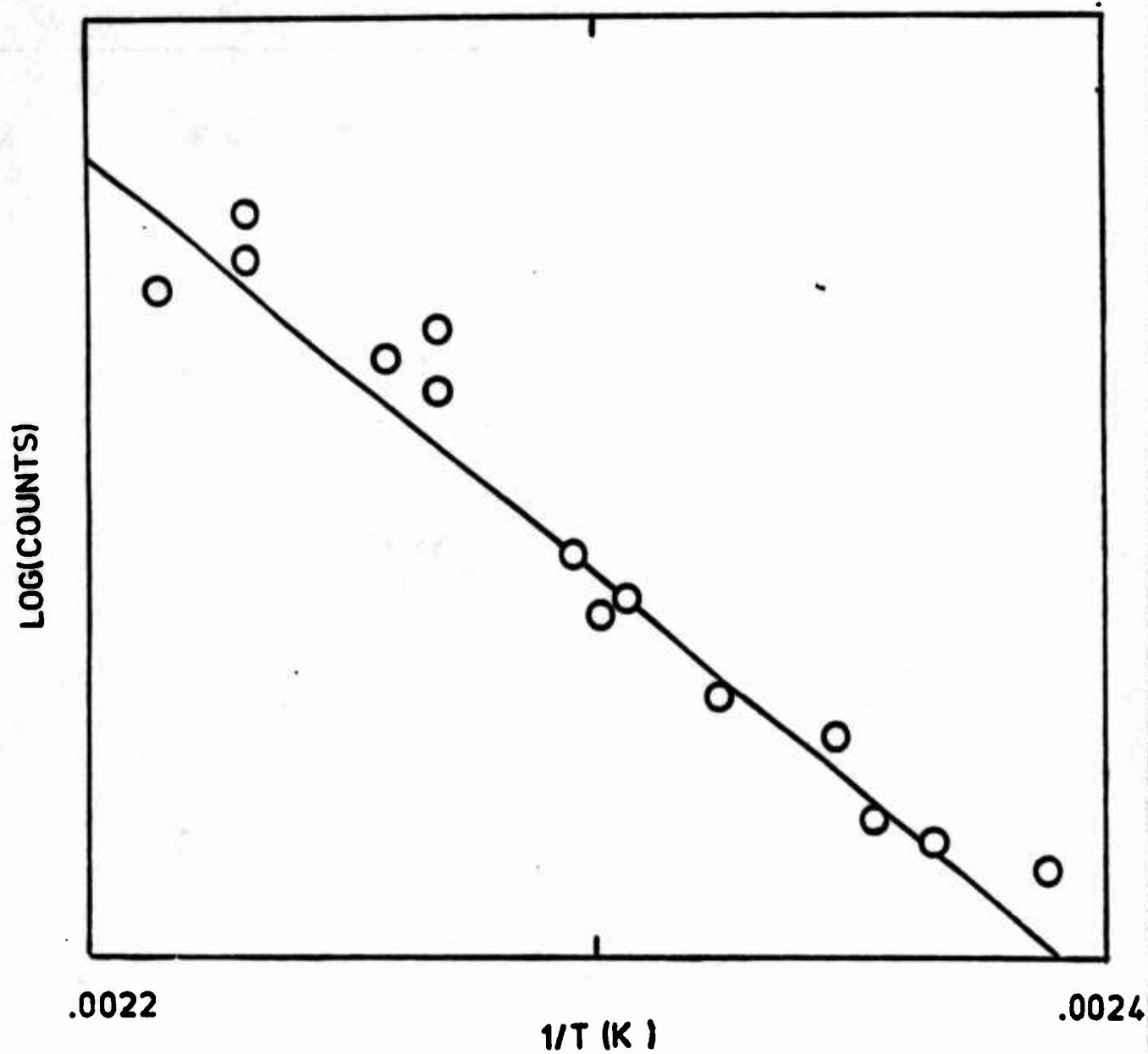


Figure 6. Activation Energy Plots in the Gated Scalar Mode (Concluded)

(d). Ion Mass = 46

Table II. Activation Energy, E_M

ion mass, M (amu)	E_M (kcal/mole)	Figure
30	34.4 ± 0.8	6(a)
41	33.3 ± 4.7	6(b)
43	23.0 ± 1.2	6(c)
46	26.5 ± 1.7	6(d)

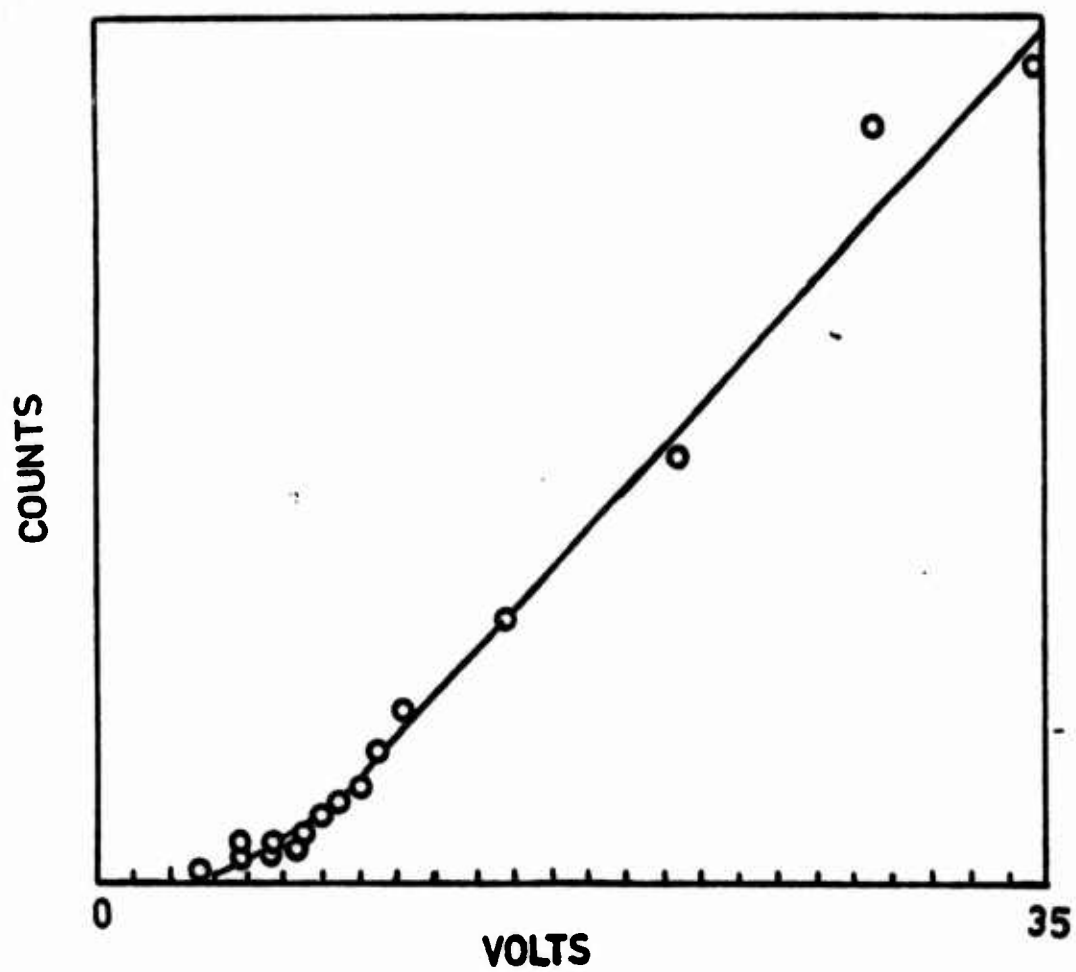


Figure 7. Appearance Potential Plots: Gated Scalar Mode

(a) Ion Mass = 30, $E_{30} = 13.0 \pm 0.5$ ev

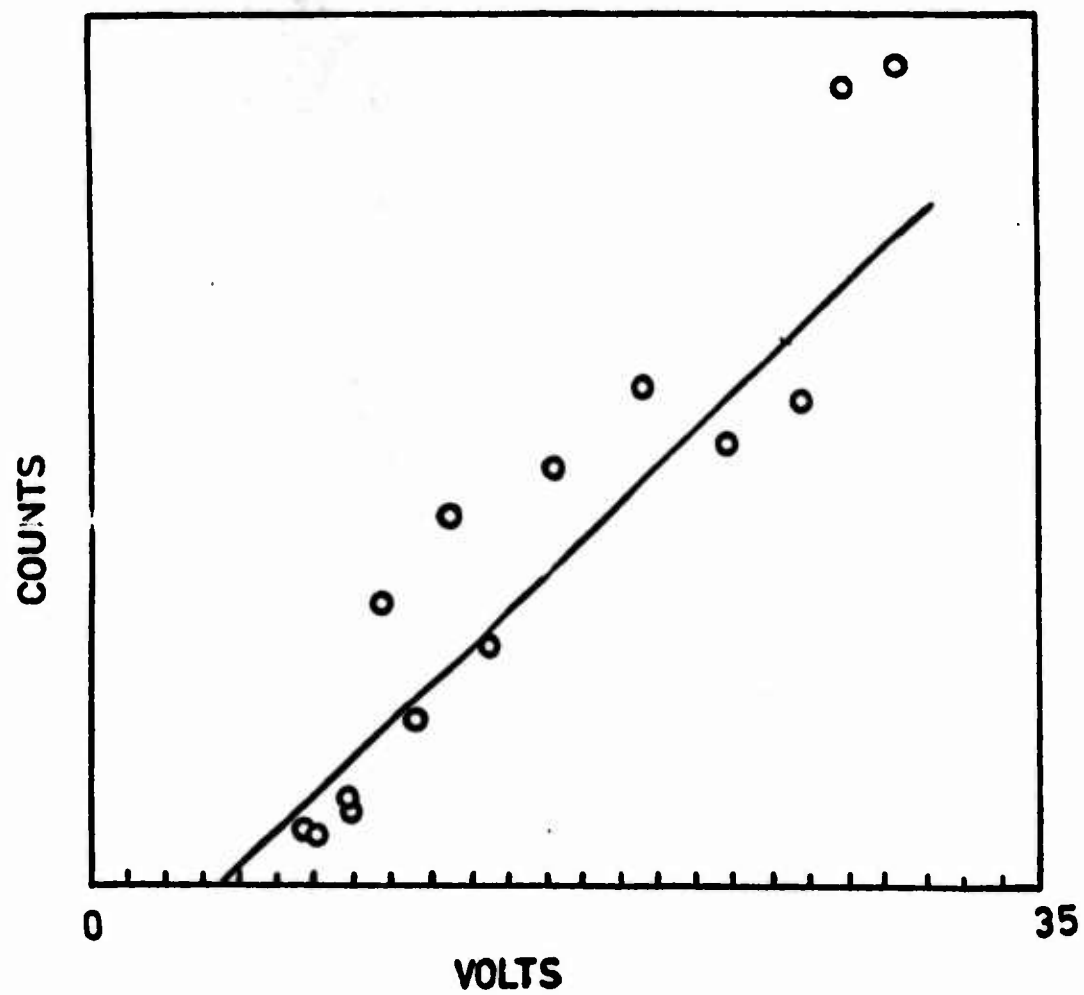
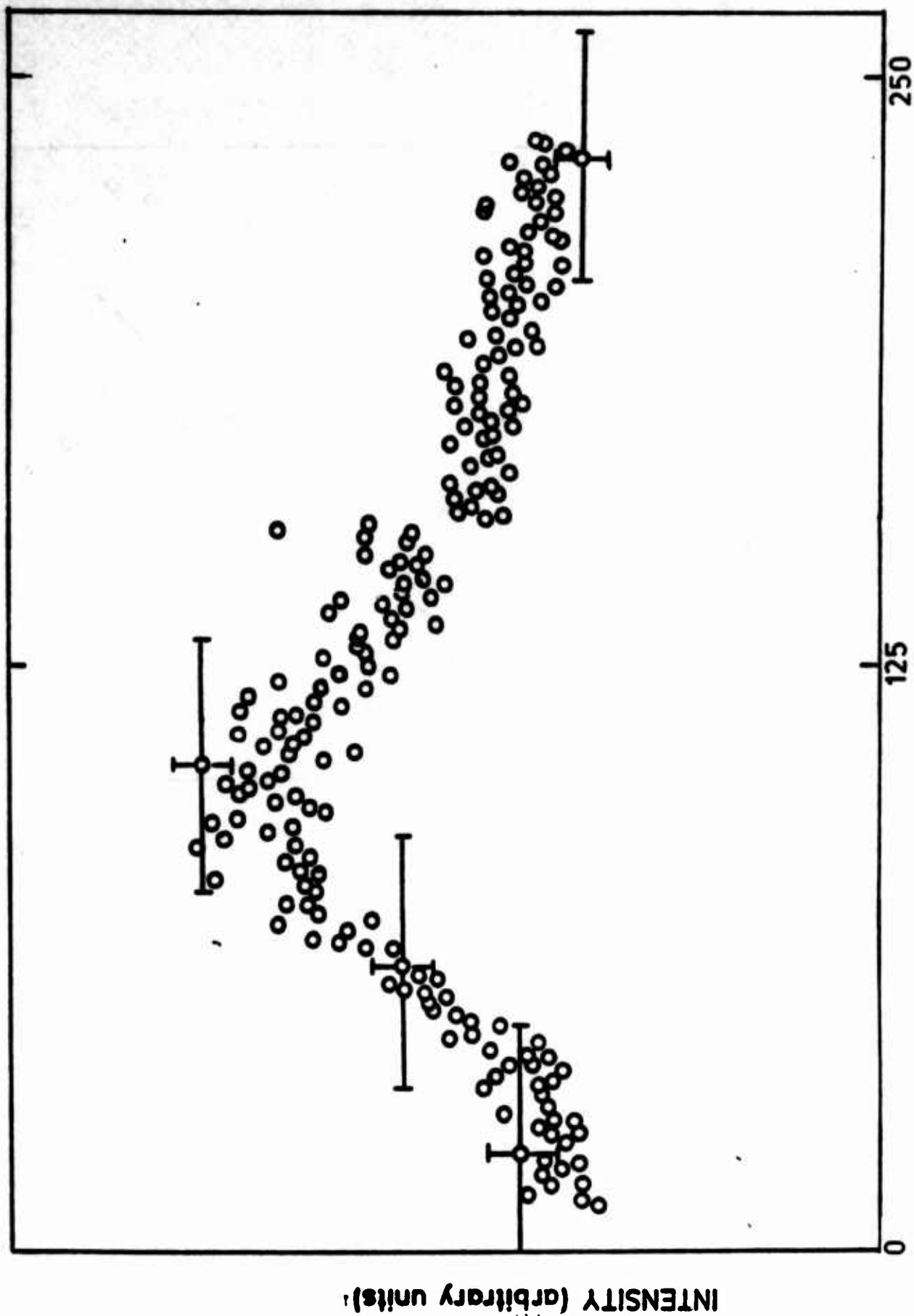


Figure 7. Appearance Potential Plot: Gated Scalar Mode (Concluded)

(b) Ion Mass = 46, $E_{46} = 13.5 \pm 1.5$ ev



CHANNEL NUMBER

Figure 8. TOF Distribution. Ion mass = 30, chopper C, 9.75 μ s/channel, reaction cell temperature = 148 $^{\circ}$ C

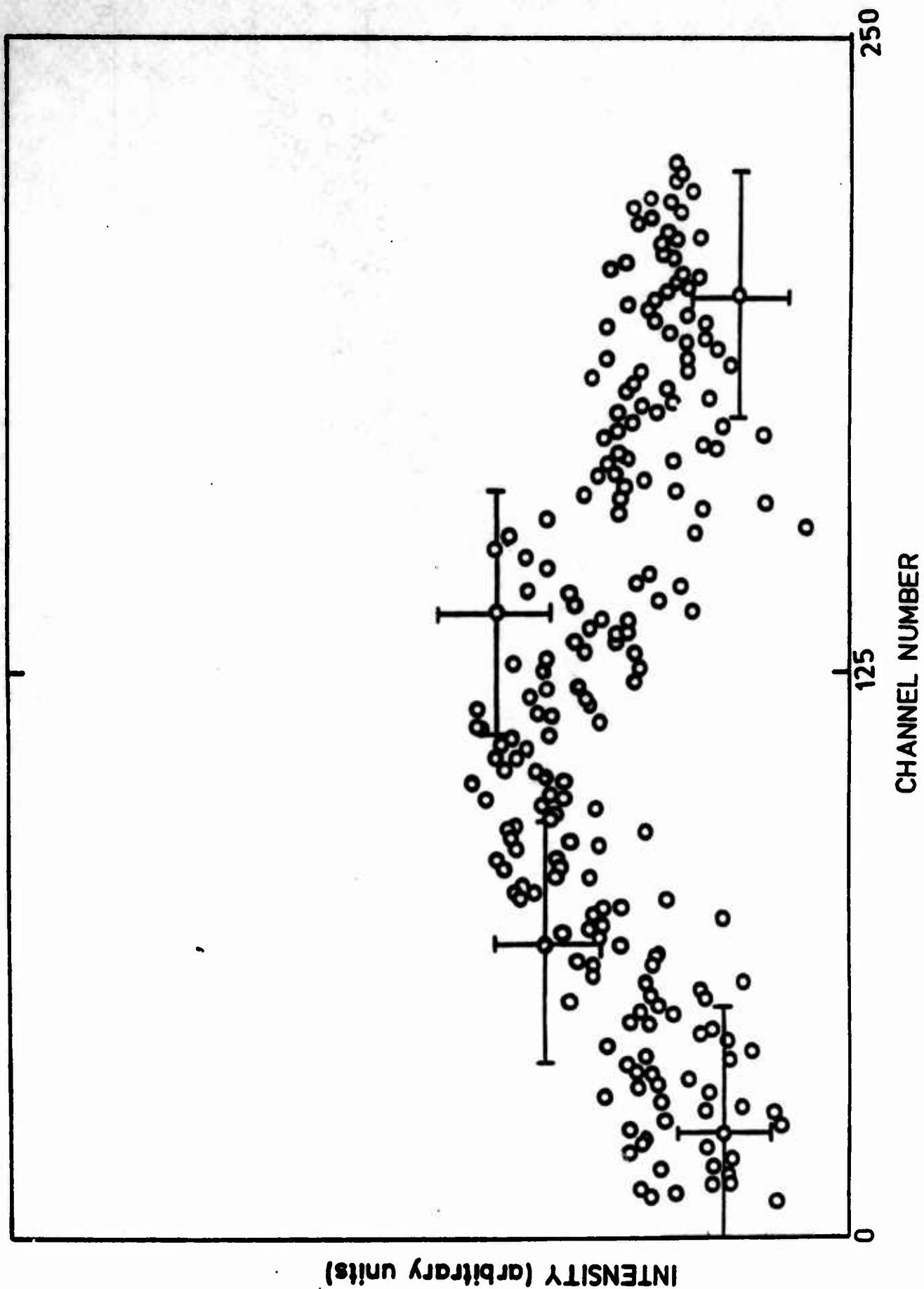
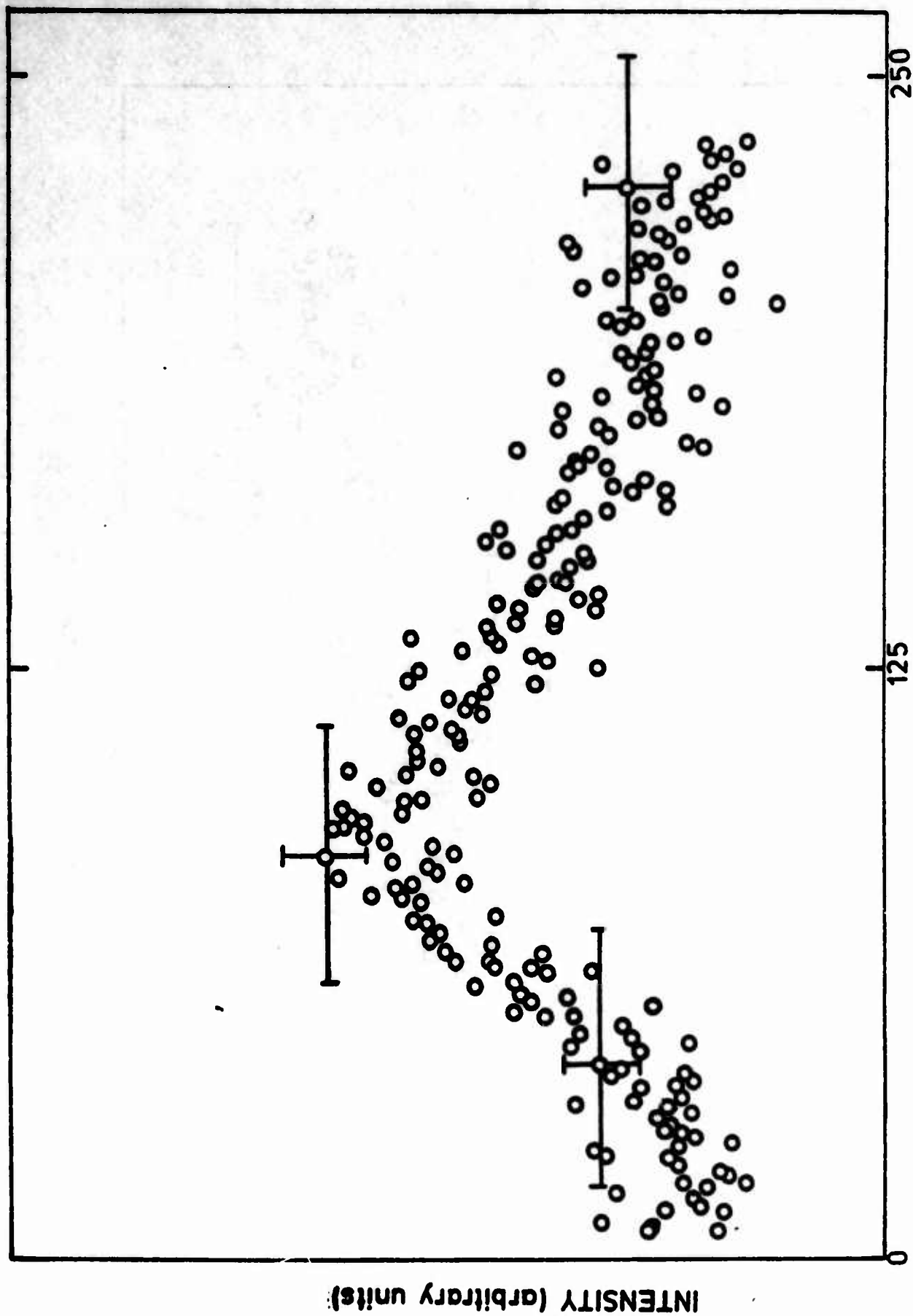


Figure 9. TOF Distribution. Ion mass = 43, chopper C, 9.75 μ s/channel, reaction cell temperature = 143°C



CHANNEL NUMBER

Figure 10. TOF Distribution. Ion mass = 46, chopper C, 9.75 μ s/channel
reaction cell temperature = 146°C

bars represent the chopper open time. The error bars shown are typical; error bars are omitted from most points for clarity. The data for ion masses of 30 and 46 have the highest signal to background ratios (see Figs.8 and 10). These two cases have been repeated with chopper B and plotted in Figs.11 and 12 with the counts in every 8 time channels added. This improves the counting statistics and since the chopper open time for these runs is equivalent to approximately 11 channels, the time resolution is not degraded. The linear least squares best fits of Eq.(1) to the data are also shown in Figs.11 and 12. The resulting values of I_i for each ion mass are summarized in Table III. Two possible fits are reported for ion mass 46. In the first, 10 product masses were initially selected ($m_i = 46, 55, 65, 75, 85, 95, 105, 115, 125$ and 135 amu) and fits were computed by linear least squares. When negative (nonphysical) I_i 's were obtained, those masses were dropped from consideration and the fit recomputed. This procedure led to two masses, 46 and 115 which gave the best fit shown in Fig.12(a). The second fit was obtained by varying a single mass to get a best fit. The result, $m = 63$, is shown in Fig.12(b).

A limited amount of data were taken using the double oven configuration (Fig.1(b)). It was all taken using the lock-in amplifier measurement system. The reaction cell temperature was varied from 265 to 315 C and the source oven was varied from 94 to 137 C. Little variation in the relative spectra was noted over these temperature ranges; the mass spectrum presented in Fig.13 was typical.

As a check on our mass spectrometric method and to obtain data over a mass range beyond the capability of our instrument, FAB and EI spectra from Washington State University are also reported.¹⁴ The FAB

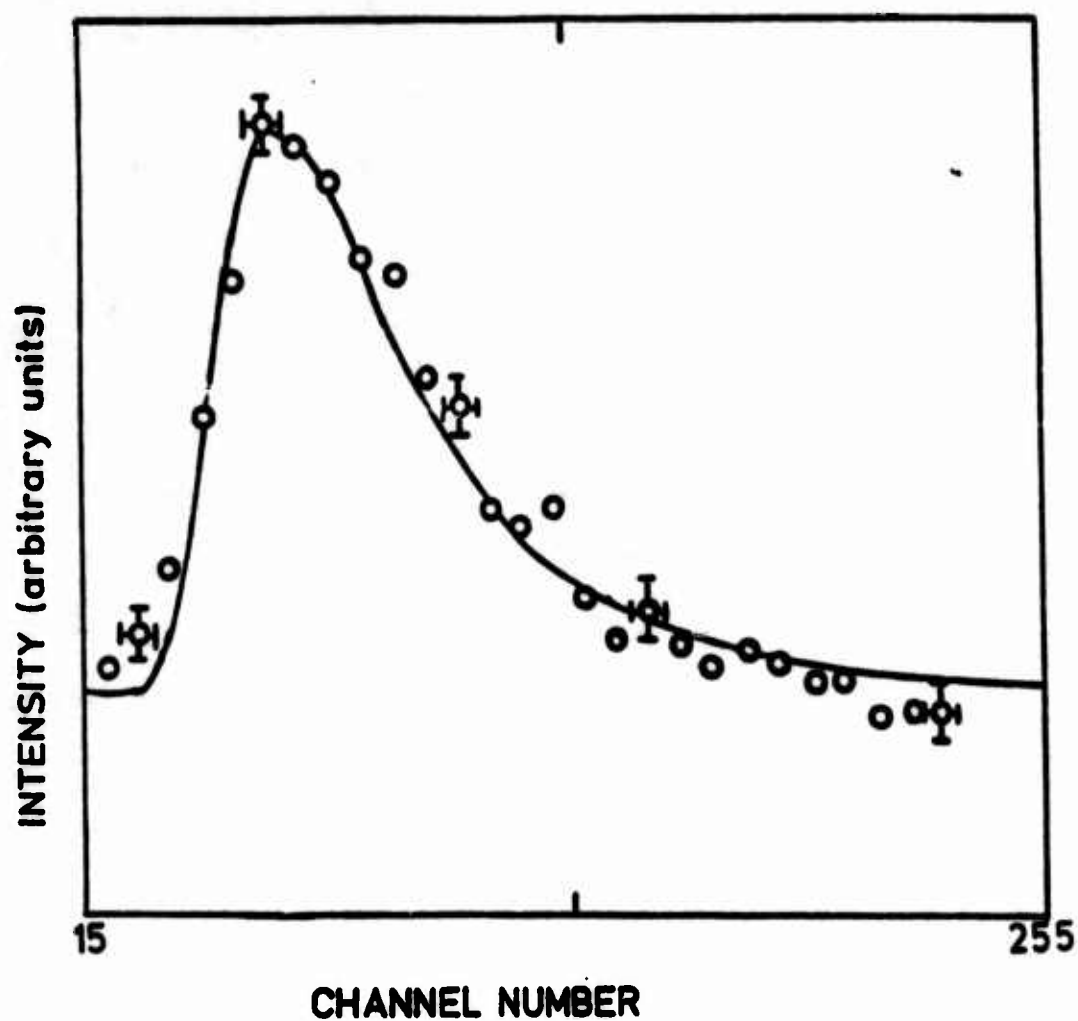


Figure 11. TOF Distribution: Ion mass = 30, chopper B, 9.75 μ s/channel, reaction cell temperature = 143°C. Curve fitted is Eq. (1) fitted with parameters given in Table III

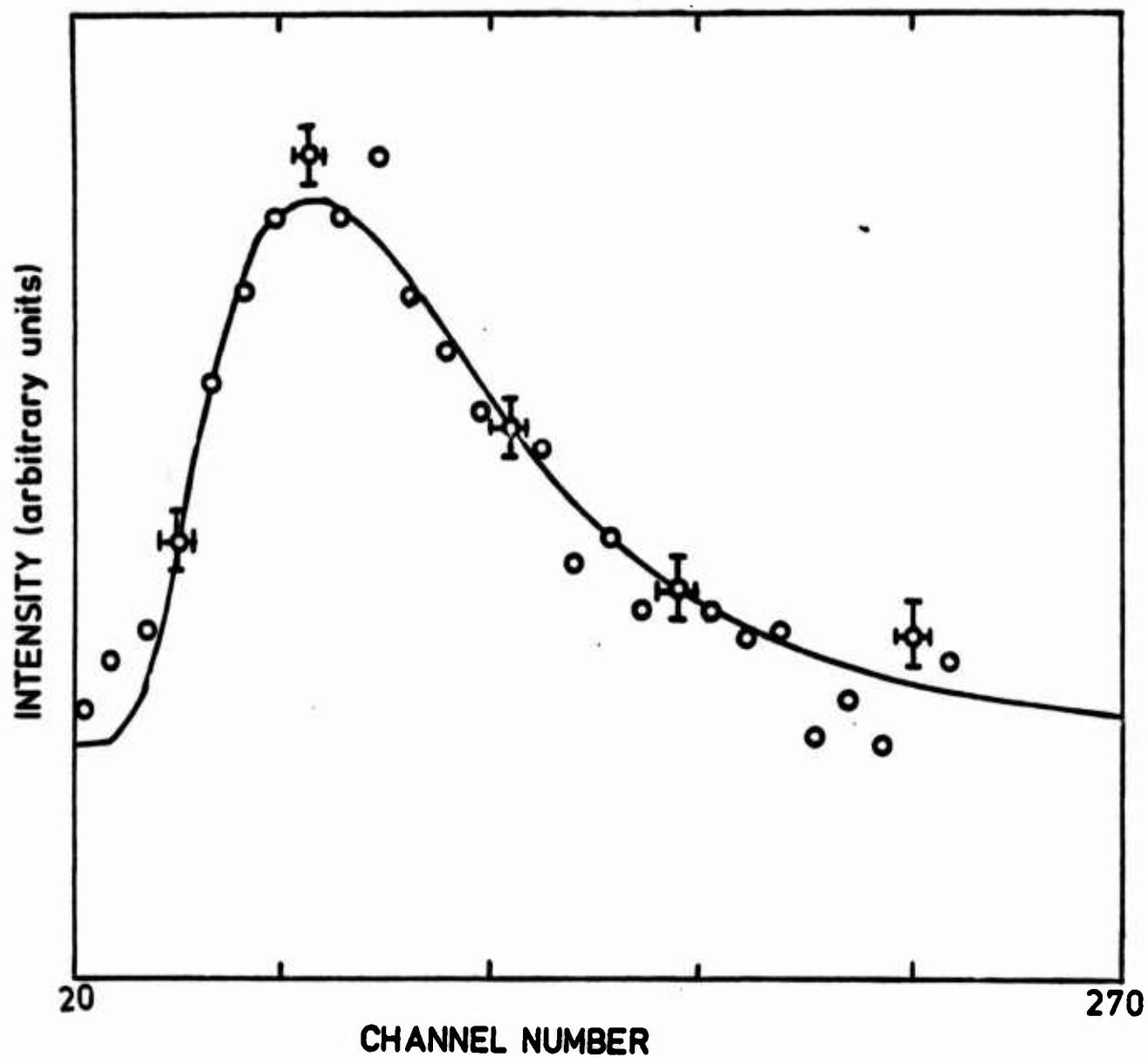


Figure 12. TOF Distribution: Ion mass = 46, chopper B, 9.75
 $\mu\text{s}/\text{channel}$, reaction cell temperature = 147 $^{\circ}\text{C}$. Curve fitted
 is Eq.(1) fitted with parameters given in Table III
 (a). Two products

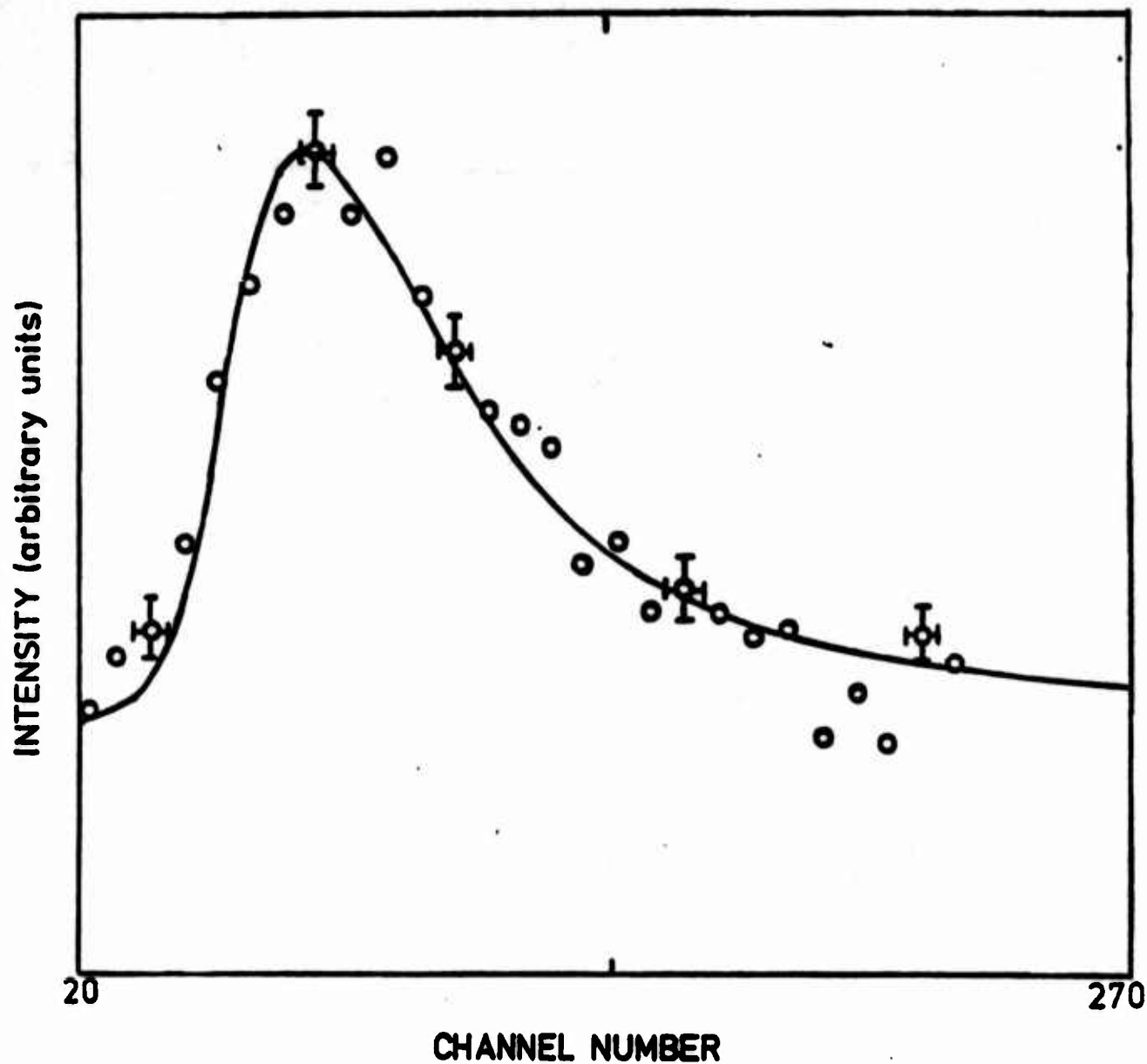


Figure 12. TOF Distribution: Ion mass = 46, chopper B, 9.75

$\mu\text{s/channel}$, reaction cell temperature = 147°C . Curve fitted
is Eq.(1) fitted with parameters given in Table III (Concluded)
(b). Single product

Table III. Eq.(1); best fit parameters

N	M (amu)	m_1 (amu)	$I_1 \times 10^5$	Figure
1	30	46	3.31 ± 0.09	11
2	46	46	2.98 ± 0.14	12(a)
		115	11.58 ± 0.81	12(a)
1	46	63	7.63 ± 0.24	12(b)

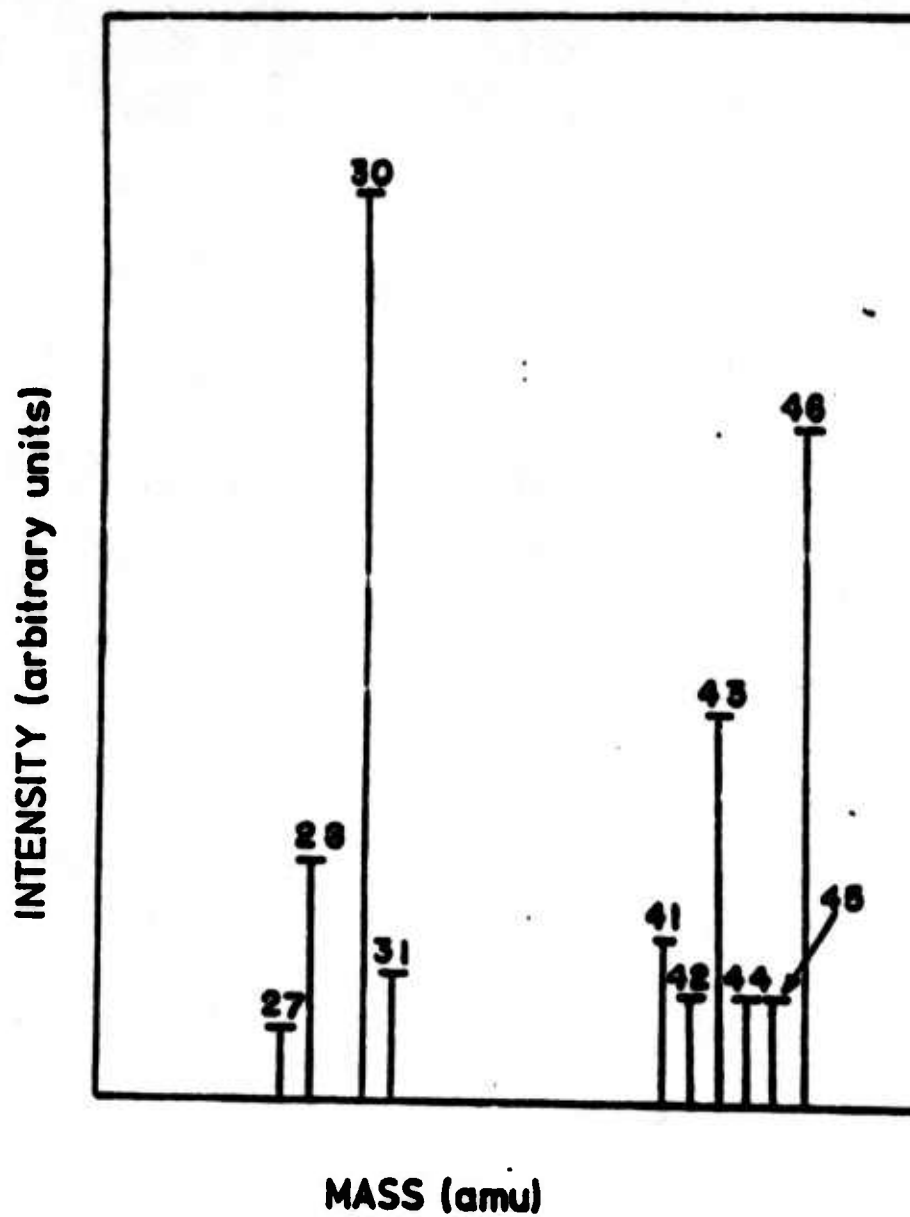


Figure 13. BDD Mass Spectrum. Double oven configuration (Fig. 1(b),
lock-in amplifier measurement, reaction cell temperature =
265 °C, source cell temperature = 109 °C

spectrum is presented in Fig.14 and the EI spectrum in Fig.15. A chromatogram run on the EI machine is presented in Fig.16 for ion masses of 30,46 and 57 amu as well as the total ion signal. During these runs the BDD sample was heated and each scan took approximately 2 sec.

In addition to the the mass spectrometric studies, an in vitro heating experiment was affected. The BDD (100mg) was heated under vacuum (0.1 Torr with continual pumping) in an oil bath (160-170 C) for five hours. The solid melted to form a colorless liquid, which bubbled moderately throughout. The solid white residue was analyzed by FAB mass spectrometry¹⁴ and Fourier transform IR¹² and found to be identical to the initial BDD.

During the course of the experimental program it was noted that a white residue accumulated on our chopper wheels. This residue was also analyzed by using the FAB mass spectrometer¹⁴ and its spectrum was identical to the BDD FAB mass spectrum.

V. Discussion

The data show that on heating BDD, the four most abundant ions exhibiting time dependent behavior in our modulated beam machine have masses of 30,46,43 and 41 amu. The TOF analysis reveals that: (i) The 30 amu ion is primarily a fragment of a 46 amu product of thermal decomposition and (ii) the 46 amu ion is either a fragment from a single product species with a mass of approximately 63, or it is generated in the ion source by two decomposition products, one with a mass of 46 amu and another with an approximate mass of 115 amu. The 43 and 41 amu ions were not sufficiently abundant to affect the TOF analysis. These results can be interpreted as representing a thermal

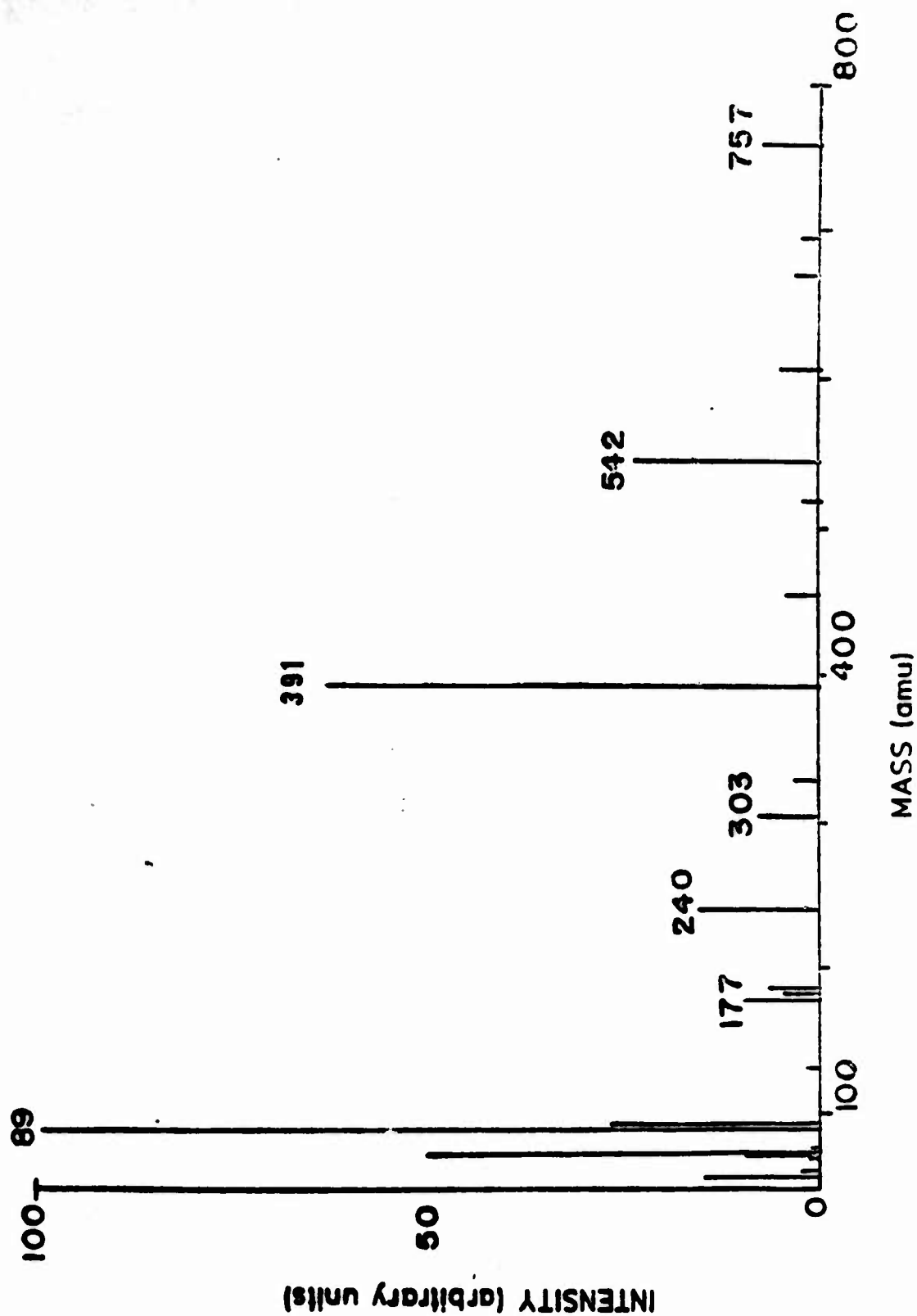


Figure 1). FAB Mass Spectra of BDD (Washington State Univ.)

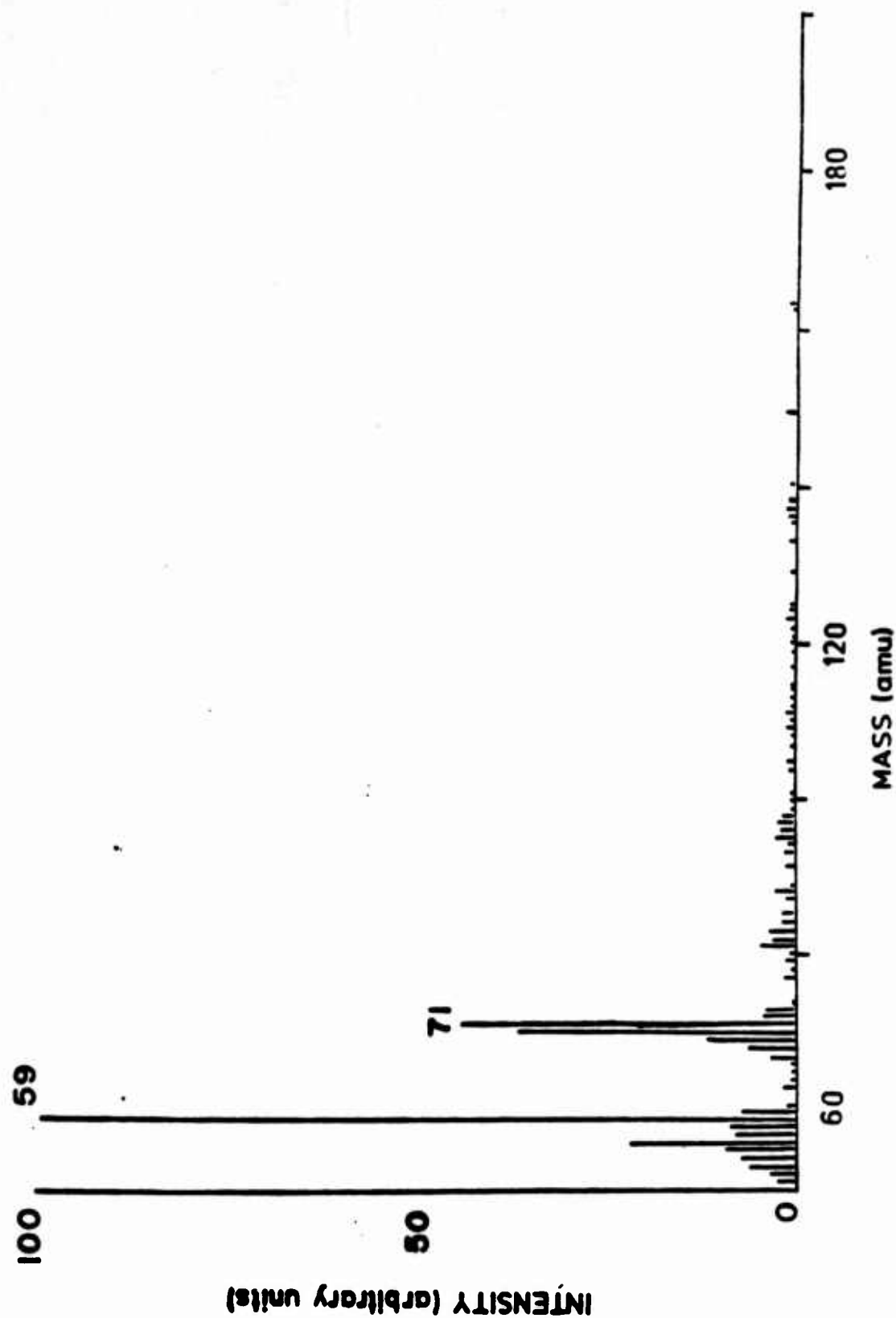


Figure 15. EI Mass Spectra of BDD (Washington State Univ.)

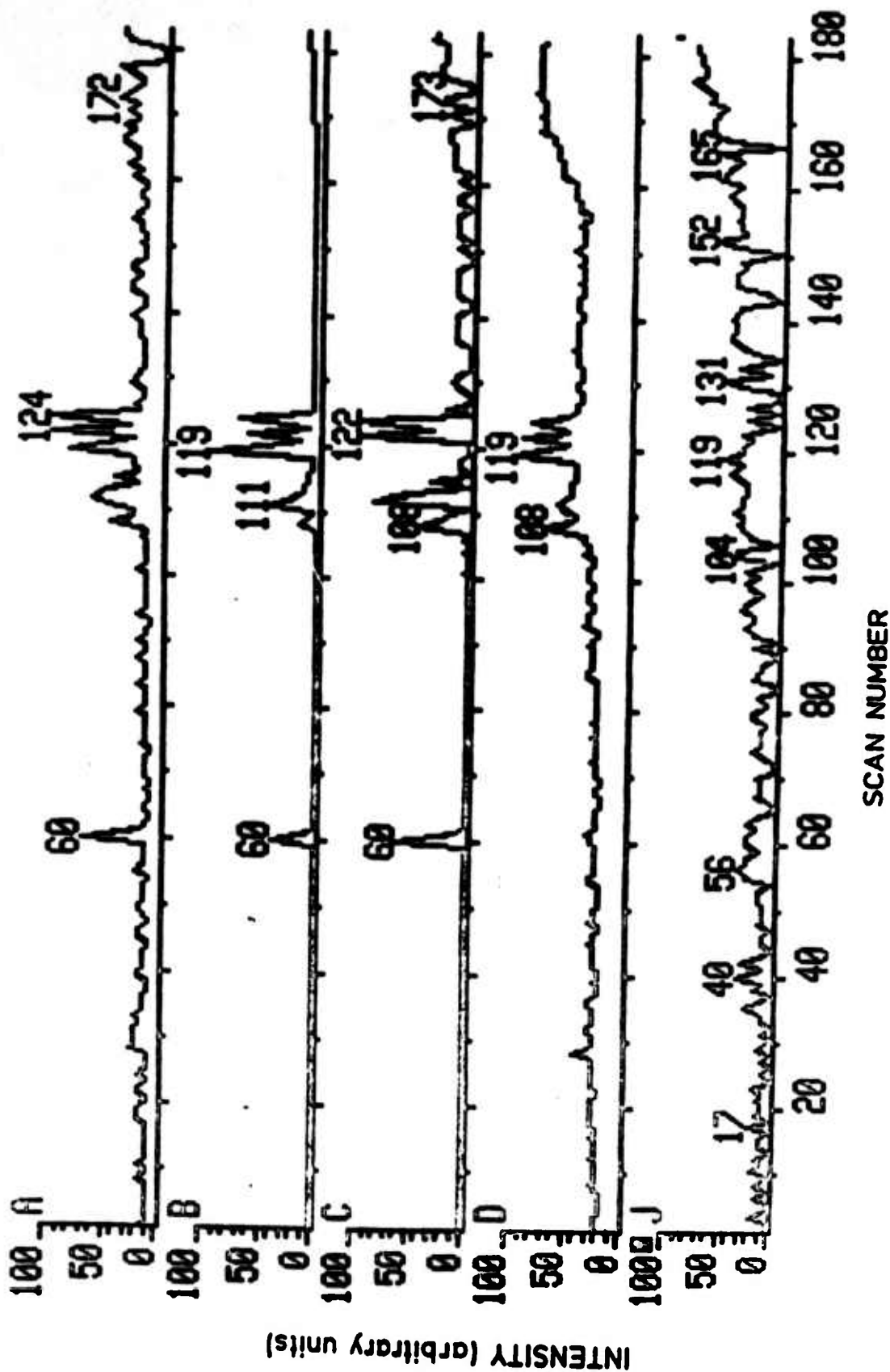
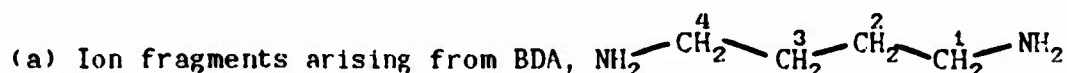


Figure 16. EI Chromatogram of BDD. Approximately 2 sec./scan. A, total ion current; B, ion mass 46, 1.85×10^7 total counts; C, ion mass 30, 10.54×10^7 total counts; D, ion mass 57, 2.07×10^6 total counts; H, ion mass 446 (pump oil), 2.27×10^5 total counts

dissociation of BDD into HNO_3 and BDA (1,4-butanediamine). The standard EI mass spectrum¹⁵ of NO_2 shows NO as the major fragment ion, which supports this postulation. It is most likely that the NO_2 is formed by decomposition of HNO_3 in the reaction cell. The 46 amu ion signal may then represent undissociated HNO_3 , which was one of the possible fits of Eq.(1) to the TOF data.

The 43 amu ion is a significant fragment in the EI mass spectrum of BDA,¹⁵ which provides tentative support for the generation of BDA from BDD. In the EI mass spectrum of BDA there is no abundant ion > 50 amu.¹⁵ Our spectra yielded a similar result. The EI spectra obtained at Washington State University¹⁴ (Fig.15) is virtually devoid of high mass ions. Mass chromatographic analyses of the spectra confirmed the presence of 30 and 46 amu ions as major components (Fig.16). The masses, intensities and tentative molecular formulae of the major fragment ions are listed in Table IV.

The mass spectra provide evidence for the dissociation of BDD into BDA and nitric acid, although it is still unclear whether this process occurs via the mononitrate salt BDM. Possible routes to the major observed ions are shown below:



(1) Fragment ions arising from cleavage of C-N bonds

Table IV. Mass spectrometric Data for BDD

M (amu)	Ion Intensity	Probable Molecular Formula	Origin <u>via</u>
71	15507000	C_4H_9N	BDA or BDM
70	n.d.	C_4H_8N	BDA
59	28539000	C_3H_9N	EDA
57	2074000	C_3H_8N	BDA
56	n.d.	C_4H_8 ?	EDA
46	18460000	NO_2	HNO_3
30	105433000	NO ; CH_4N	BDA, HNO_3



71 amu

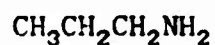


70 amu



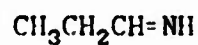
56 amu (loss of N_2H_4)

(2) Fragments arising from cleavage of $\overset{1}{\text{C}}-\overset{2}{\text{C}}$ bond



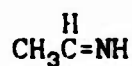
59 amu

;

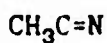
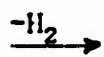


57 amu

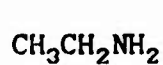
(3) Fragments arising from cleavage of $\overset{2}{\text{C}}-\overset{3}{\text{C}}$ bond



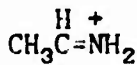
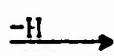
43 amu



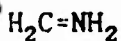
41 amu



45 amu



44 amu



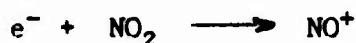
30 amu

(b) Fragments arising from cleavage of HNO_3

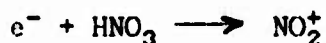
The mass spectrum of nitric acid is not readily available, e.g., it is not recorded in the N.B.S. Environmental Protection Agency files,¹⁵ however, it is well-known that nitric acid undergoes decomposition to NO_2 (46 amu), hence the 46 amu ion is attributed to nitric acid.

The high activation energy for the production of NO_2 , as evidenced by the TOF of ion mass 30 (the dominant NO_2 fragment ion¹⁵) compared to the activation energy for the production of HNO_3 as evidenced by the TOF of ion mass 46 gives further support to the above interpretation. Also, ion fragment 43 (in (a3) above) from BDA should have the same activation energy as ion 46 which represents nitric acid, the other product of BDD dissociation. From Table III it can be seen that to within experimental uncertainty we do observe ion fragments 43 and 46 to have the same activation energy.

Our appearance potential measurements indicate ions 30 and 46 are within 1.0 electron-volts, with mass 46 being slightly higher. This is in agreement with the ionization processes



and



Clearly the second process would be expected to have the higher appearance potential.

The TOF, EI and FAB mass spectral analyses of BDD all provide evidence that the initial decomposition of BDD is a dissociation into two volatile components: BDA and nitric acid. If this is a valid statement, then it follows that the residual solid from a heating experiment in which the volatile components are removed under reduced pressure should be unchanged BDD. Analysis by FAB¹⁴ and IR¹² of the residue from the heating of BDD showed that the residue was indeed BDD, thereby supporting the hypothesis.

VI. Conclusions

All of the data obtained in the present study indicate that, under vacuum, BDD thermally decomposes at temperatures in the range 160-180 C to produce BDA and nitric acid. The nitric acid partially decomposes to produce nitrogen dioxide. Since all products are volatile, the solid residue after heating is pure BDD.

THE APPENDIX

THE TOF DISTRIBUTION

Appendix : The TOF distribution

A beam effusing from a chamber containing a gas with a Maxwellian velocity distribution at temperature U has a velocity dependent intensity $J(v)$ given by

$$J(v)dv = Cv^3 \exp(-(v/\alpha)^2) dv \quad (A1)$$

where v is the molecular velocity, C is the intensity constant and $\alpha = \sqrt{2kU/m}$ with k , Boltzmann's constant, U gas temperature and m the molecular mass.

If this effusive beam is detected by electron bombardment ionization, the ionization probability (and thus the detection efficiency) is proportional to the time a molecule spends in the electron beam, and therefore is inversely proportional to molecular velocity. The detected velocity dependent beam intensity with velocity in dv at v is then given by

$$J_d(v)dv = C'v^2 \exp(-(v/\alpha)^2) dv \quad (A2)$$

where v_0/v is the detection efficiency and $C' = Cv_0$.

The velocity distribution function is converted to a time of arrival (t) distribution function by using $v = L/t$, where L is the beam path length. If the flight begins as the molecule passes through the chopper slit at time, t' , then the number of molecules passing through the chopper in dt' at t' and arriving at the detector in dt at t is given by

$$G(t, t') dt dt' = C'(t') \frac{L^3}{(t-t')^4} \exp\left(-\frac{L^2}{\alpha^2(t-t')^2}\right) \quad (A3)$$

For the chopper transmission function $C'(t')$ we take

$$C'(t') = \begin{cases} C_0 & , T \geq t' \geq 0 \\ 0 & , t' > T \end{cases}$$

where T is the chopper open time. Integration of eq. (A3) over the chopper opening gives the TOF distribution for $t > T$ gives

$$I_M(t) = I_0 \left[\frac{1}{(t-T)} \exp\left(-\frac{L^2}{\alpha^2(t-T)^2}\right) - \frac{1}{t} \exp\left(-\frac{L^2}{\alpha^2 t^2}\right) \right. \\ \left. + \frac{\sqrt{\pi}\alpha}{2L} \left\{ \operatorname{erf}\left(\frac{L}{\alpha t}\right) - \operatorname{erf}\left(\frac{L}{\alpha(t-T)}\right) \right\} \right] \quad (A4)$$

where $I_0 = C_0 L \alpha^2 / 2$ is the intensity constant. For N product masses yielding the same ion mass, M Eq. (A4) has the form

$$I_M(t) = \sum_{i=1}^N I_i f_i(t) + I_b \quad (A5)$$

where I_i is the intensity constant of the product mass m_i , I_b is the background intensity and

$$f_i(t) = \left[\frac{1}{(t-T)} \exp\left(-\frac{L^2}{\alpha_i^2(t-T)^2}\right) - \frac{1}{t} \exp\left(-\frac{L^2}{\alpha_i^2 t^2}\right) \right. \\ \left. + \frac{\sqrt{\pi}\alpha_i}{2L} \left\{ \operatorname{erf}\left(\frac{L}{\alpha_i t}\right) - \operatorname{erf}\left(\frac{L}{\alpha_i(t-T)}\right) \right\} \right].$$

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